

Contaminant Transport through Subsurface Material from the D.O.E. Hanford Reservation

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Introduction

The U.S. Department of Energy's Hanford Reservation is a nuclear materials processing facility located in the Columbia River Basin in south central Washington. The area receives an average annual rainfall of ~16 cm/year and depth to groundwater averages around 100 m across the site. The vadose zone is composed of sediments from the Hanford Formation, the Plio-Pleistocene Unit, and the Ringold Formation at the groundwater interface (Fig. 1). Processing waste has historically been disposed of in cribs, solid waste burial pits, ponds, and/or underground storage tanks which reside within the Hanford Formation. The most concentrated wastes were stored in single-shelled tanks in the 200 area of the Hanford Site [1,2]. About one-third of the tanks in the 200 Area have leaked resulting in more than 1 million gallons of hazardous and radioactive waste in the vadose zone. Relatively mobile radionuclides such as ⁹⁹Tc, ¹²⁹I, U, and ³H have traveled further than predicted and have been detected in the groundwater, which eventually flows to the Columbia River [3,4]. This has suggested that contaminant migration through the vadose zone at Hanford is accelerated and the mechanisms remain unclear.

The goal of this study is to provide an improved understanding and predictive capability of the geochemical mechanisms that influence the migration of contaminants in the Hanford vadose zone. The objectives are to use sorption isotherms and miscible displacement experiments to investigate the interactions of various radionuclides and heavy metals such as U(VI), Sr, Cs, Co, and Cr(VI) with Hanford subsurface media. The effects of variations in ionic strength, pH, and the presence of competing cations have been investigated for the various radionuclides and toxic metals. The results of this study will improve our understanding of the rates and mechanisms of the transport of radionuclides and toxic metals through the Hanford vadose zone.

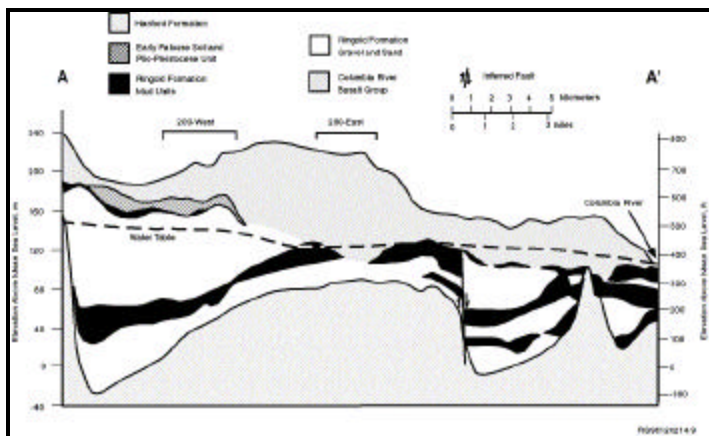


FIGURE 1.

Material and Methods

Disturbed geologic media was collected from the Hanford formation, the Plio-Pleistocene unit, and the Upper Ringold formation. The Hanford formation comprises the upper 45 m of the vadose zone and is a Pleistocene age flood deposit formed from the flood of the glacial Lake Missoula to the east [2, 5]. It is a heterogeneous, unconsolidated laminated coarse and fine sand unit interbedded with small-scale clay layering (Fig. 2). Boulder- and gravel-sized rocks are intermixed to create a highly heterogeneous particle size distribution. The Plio-Pleistocene unit averages 11 m in thickness and is highly cemented and calcarious in nature as a result of insitu weathering of the Upper Ringold formation [2]. The Upper Ringold comprises the lower 11 m of the vadose zone and consists of semi-consolidated, laminated fine-grained silts and sands deposited in a lacustrine environment (Fig. 3).

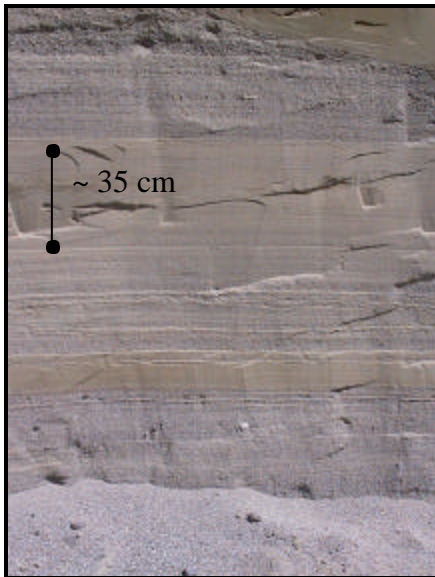


FIGURE 2



FIGURE 3

Batch sorption isotherm and miscible displacement experiments were conducted using reactive tracers U(VI), Sr, Cs, Co, and Cr(VI). Both batch and miscible displacement experimental techniques were used to investigate the effects of variations in pH and ionic strength, and competing cations on geochemical interactions with subsurface media. Transport experiments were used to determine the reversibility of sorption processes and the effects of flow. Batch isotherm experiments were carried out in 30 cm³ polyethylene centrifuge tubes using 2 g of geologic media and 4 ml of solution containing reactive tracers. The tubes were then placed on a shaker for 72 hrs. Solutions contained a reactive tracer(s) in NaNO₃ with varying ionic strength. For the U(VI) solution, the pH was adjusted with NaHCO₃ and 1% CO₂(g). The increased level of CO₂(g) was not only representative of subsurface CO₂(g) levels, but also necessary to increase uranium solubility and form a stable U-carbonate complex. U(VI) batch experiments were conducted in a glove box with a 1% CO₂(g) atmosphere. Batch experiments were used to determine sorption coefficients (K_d) for U(VI), Sr, Cs, Co, and Cr(VI) interactions with subsurface media. Column experiments were conducted in a glass column 4.5 cm in length and 1 cm in diameter packed with saturated media. The solution used for all column experiments contained a nonreactive tracer (Br⁻) and reactive tracer(s) in a 0.1 M NaNO₃. A medical pump was used to deliver solution to the column at an average flow rate of ~2 cmhr⁻¹. Effluent solution was collected in tubes on a fraction collector.

Results and Conclusions

Our results indicate that the geochemical mechanisms governing contaminant interactions with subsurface media were influenced by changes in solution chemistry such as ionic strength, pH, presence of competing cations, and the dynamics of flow. Variations in ionic strength influenced the sorption of Sr and Cs while these effects were minimal for U(VI). When ionic strength was increased, sorption of Sr and Cs decreased which suggests the mechanism of sorption was cation exchange. The transport of Sr was not affected by the presence of trace competing cations (Cs) in either the Hanford or Ringold media. In contrast, the transport of Cs was affected by the presence of Sr, as seen in an increase in retardation. This was only observed in the Hanford formation, which suggests that mineralogical differences may account for this observation. It is believed that biotite mica, present in the Hanford, is more reactive with Cs [6, 7, 8]. The sorption of strontium and cesium increased under flowing conditions possibly due to the larger rock / water ratio in the column as compared to batch experiments (Fig. 4).

Batch isotherms show that as solution pH increases, U(VI) sorption decreases (Fig. 5). This is most likely due to the formation of $\text{UO}_2(\text{CO}_3)_3^{4-}$ at pH 8 and $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ at pH 7 [9, 10, 11]. The species may have different affinities for the subsurface media as indicated by the delayed breakthrough at pH 7 vs pH 8 (Fig. 6). Uranium sorption decreased under flowing versus equilibrium conditions, which is suggestive of kinetic effects on uranium sorption. The large uranium carbonate complex may be sterically hindered from interacting with all of the available sorption sites.

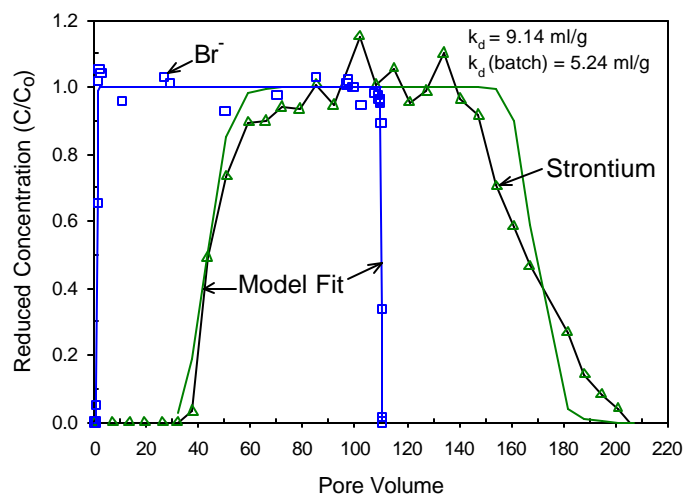


FIGURE 4

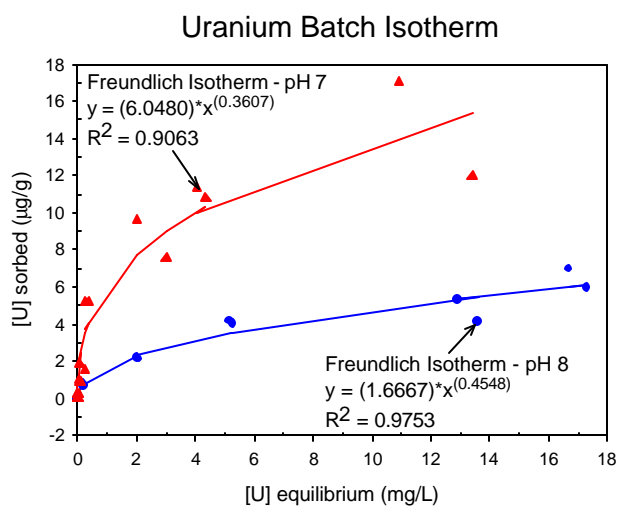


FIGURE 5

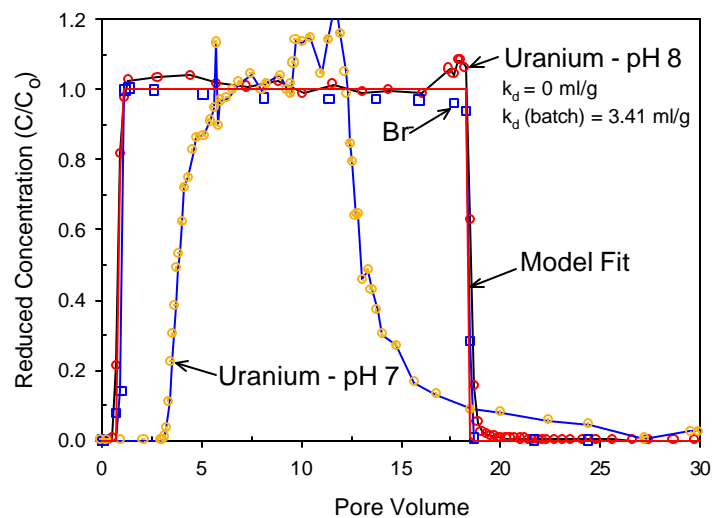


FIGURE 6

Current results suggest that sediment characteristics such as mineralogy, iron content, organic matter, and cation / anion exchange capacity coupled with the dynamics of flow impact the number of sites available for sorption. Similar batch and column experiments using Co and Cr(VI) are currently under investigation. Investigative approaches using a combination of batch and transport experiments will contribute to the conceptual and quantitative understanding of contaminant mobility in the Hanford vadose zone.

References

1. Agnew, S. F., J. Boyer, R. A. Corbin, T. B. Duran, J. R. Fitzpatrick, K. A. Jurgensen, T. P. Ortiz and B. L. Young. 1997. Hanford tank chemical and radionuclide inventories: HDW Model, LA-UR-96-3860, Rev. 4, Los Alamos National Laboratory, Los Alamos, NM.
2. Bjornstad, B.N. 1990. Geohydrology of the 218-W-5 burial ground, 200-west area, Hanford site. PNNL-7336, Pacific Northwest National Laboratory, Richland, WA.
3. Dirkes, R. L., and R. W. Hanf. 1997. Hanford site environmental report for calendar year 1996, PNNL-11472, Pacific Northwest National Laboratory, Richland, WA.
4. Hartman, M. J., and P. E. Dresel. 1997. Hanford site groundwater monitoring for fiscal year 1996, PNNL-11470, Pacific Northwest National Laboratory, Richland, WA.
5. Lindsey, K.A. 1995. Miocene- to Pliocene-aged suprabasalt sediments of the Hanford site, south-central Washington. BHI-00184, Bechtel Hanford, Inc., Richland, WA.
6. Roh, Y., M.A. Mayes, M.N. Pace, and P.M. Jardine. 200_. (in prep)
7. McKinley, J.P., C.J. Zeissler, J.M. Zachara, R.J. Serne, R.M. Lindstrom, H.T. Schaef, and R.D. Orr. 2001. Distribution and retention of ¹³⁷Cs in sediments at the Hanford Site, Washington. Environ. Sci. Technol. 35(17), 3433-3441.
8. Zachara, J.M., S.C. Smith, C. Liu, J.P. McKinley, R.J. Serne, and P.L. Gassman. 2002. Sorption of Cs⁺ to micaceous subsurface sediments from the Hanford site, USA. Geochim. Cosmochim. Acta 66(2), 193-211.
9. Bostick, B.C, M.O. Barnett, P.M. Jardine, S.C. Brooks, S.E. Fendorf. 2002. Uranyl surface species formed on subsurface media from DOE facilities. Soil Sci. Soc. Am. J. 66:99-108.
10. Barnett, M.O., P.M. Jardine, S.C. Brooks. 2002. U(VI) adsorption to heterogeneous subsurface media: Application to a surface complexation model. Environ. Sci. Technol. 36(5), 937-942.
11. Pace, M.N., M.A. Mayes, P.M. Jardine, X. Yin, T.L. Mehlhorn, and J.M. Zachara. 2002. Soil Science Society of American National Meeting, Nov. 10-14, Indianapolis, IN.